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Synthesis and Characterization of Phosphorus-Containing Polyamides and Copolyamides Based on 1-[(Dialkoxyposphinyl) Methyl]-2,4- and -2,6- Diaminobenzenes

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SYNTHESIS AND CHARACTERIZATION OF PHOSPHORUS-CONTAINING
POLYAMIDES AND COPOLYAMIDES BASED ON
1-[(DIALKOXYPHOSPHINYLMETHYL)-2,4- AND -2,6-DIAMINOENZES

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SUMMARY

Phosphorus-containing polyamides and copolyamides were prepared from 1-[(dialkoxyphosphinyl)methyl]-2,4- and -2,6-diaminobenzenes. The polymers produced were characterized by infrared and proton nuclear magnetic resonance spectroscopy, differential scanning calorimetry, and thermogravimetric analysis. Their thermal properties were compared with those of the corresponding common polyamides. In addition, by determining the limiting oxygen index value of some of these polyamides, their fire-resistance was evaluated.

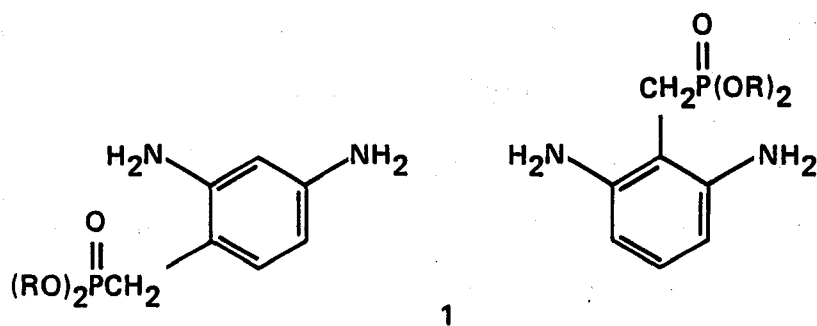
INTRODUCTION

Structurally modified polyamides have been synthesized to improve their thermal and thermal-oxidative stability (ref. 1). This approach involves the synthesis of polyamides and copolyamides from monomers bearing certain elements or groups that are effective as part of fire-retardant or thermal-stabilizing additives. The efficiency of such elements or groups is likely to be higher when they are present as an inherent part of the polymer chain, rather than as a component of a physical mixture.

The most interesting monomers for the synthesis of structurally modified polyamides are those containing phosphorus. A large number of phosphorus-bearing diacids and diamines have been successfully used to prepare fire-retardant or thermally stable polyamides (refs. 2-15).

The present work is concerned with the synthesis and characterization of fire-resistant polyamides and copolyamides prepared from 1-[(dialkoxyphosphinyl)methyl]-2,4- and -2,6-diaminobenzenes (R.1). These compounds were synthesized by nitration and subsequent catalytic hydrogenation of the corresponding (dialkoxyphosphinyl)methyl benzenes. Infrared (IR) and proton nuclear magnetic resonance (¹H-NMR) spectroscopy indicated that the product consisted of about 90% 2,4-diamino and 10% 2,6-diamino isomers (J. A. Mikroyannidis, manuscript in preparation).

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1a: R = CH₃CH₂ (DEPD)

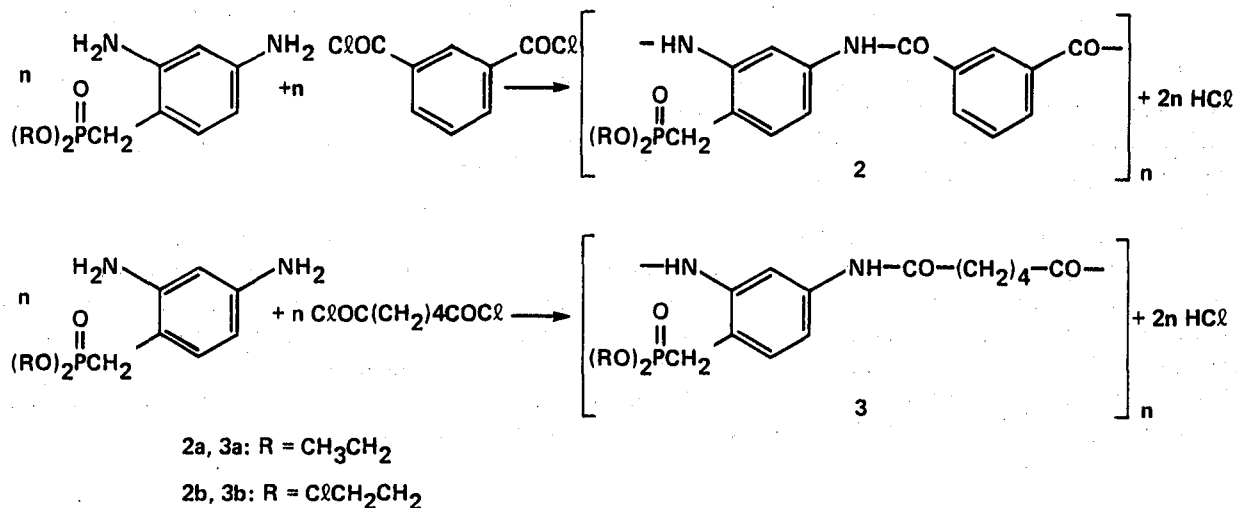
1b: R = ClCH₂CH₂ (DCEPD)

A separation of the above isomers is not necessary for many purposes. A mixture of these isomers was therefore used as starting material for preparing the phosphorus-containing polyamides.

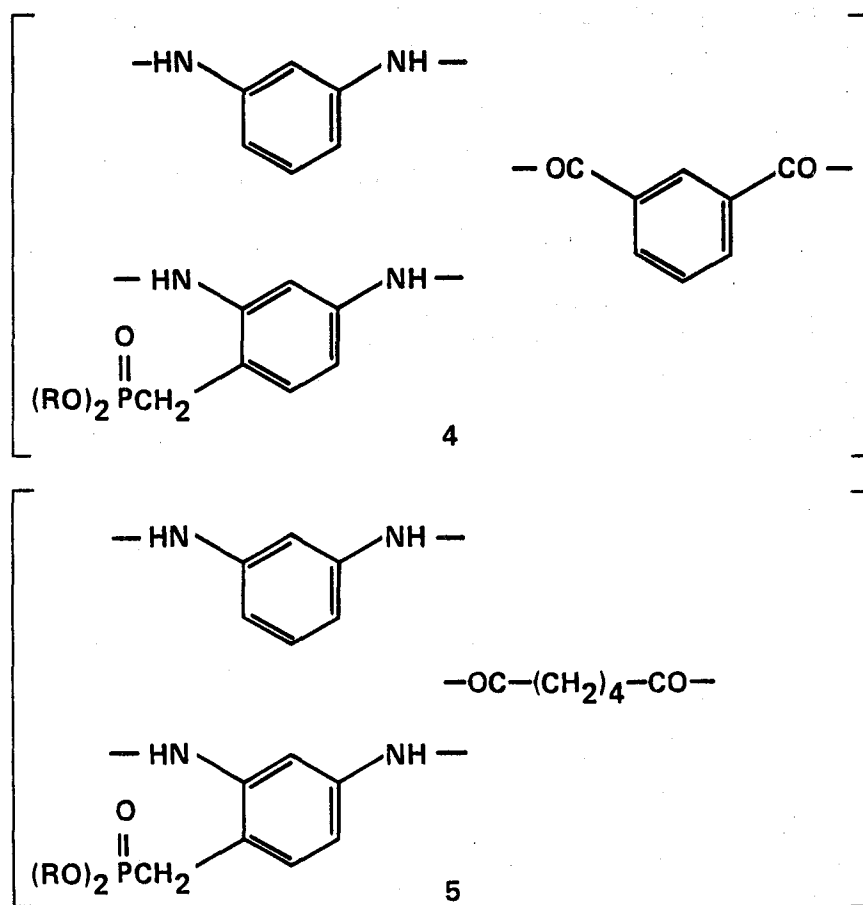
RESULTS AND DISCUSSION

Synthesis

The synthesis of the phosphorus-containing polyamides was carried out by reacting (R.1) with an acid chloride, such as isophthaloyl dichloride or adipoyl dichloride. The reaction of 1-[dialkoxyphosphinyl)methyl]-2,4-diaminobenzene, which is the predominant isomer in the synthesized compound (R.1), with an acid chloride is shown as follows:



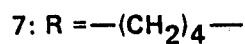
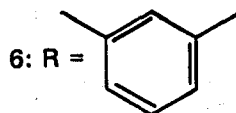
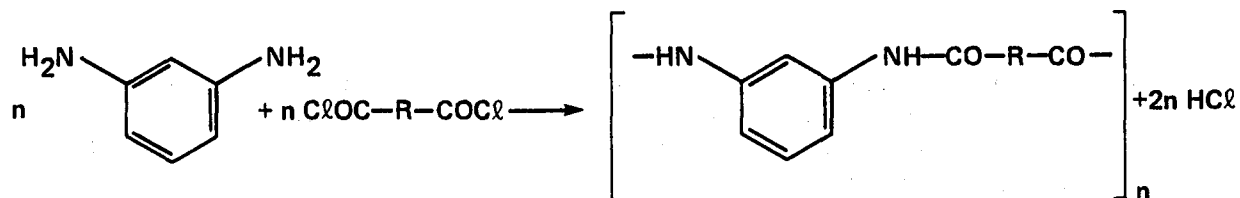
Furthermore, random copolyamides were prepared by reacting (R.1) and m-phenylenediamine with an acid chloride. The copolyamides synthesized may be represented by the following chemical structures:



4a, 5a: R = CH₃CH₂

4b, 5b: R = Cl CH₂CH₂

In addition, the following common polyamides were prepared for comparative purposes by reacting m-phenylenediamine with an acid chloride under identical experimental conditions:



The aforementioned reactions occur rapidly under mild conditions in the presence of an acid acceptor such as pyridine. The most preferred solvent is N,N-dimethylacetamide (DMAC).

Elemental Analysis and Spectroscopy

The structure of the polyamides was verified by elemental analysis (table 1), and IR and ^1H -NMR spectroscopy (table 2). The IR spectra of the phosphorus-containing polyamides indicate that the intensity of the $\text{P}=\text{O}$ stretching frequency at $1247\text{--}1215\text{ cm}^{-1}$, and the P-O-C absorption band at $1079\text{--}961\text{ cm}^{-1}$, increases progressively with increasing concentration of phosphorus moieties in polymers.

It is impossible to assign the signals caused by the secondary amide protons in the ^1H -NMR spectra of polyamides. This could, perhaps, be a result of the fast exchange of these protons with the solvent or with the traces of moisture associated with the solvent.

The polyamides 2a, 2b and 3a, 3b have low molecular weights, as indicated from their values of inherent viscosity (η_{inh}) (table 3). The copolyamides 4a, 4b and 5a, 5b have comparatively higher molecular weights. The common polyamides 6 and 7, prepared under identical experimental conditions, show the highest molecular weights. These viscosity data suggest that the molecular weights of the polyamides are reduced when their concentrations are increased in the phosphorus moieties. The low molecular weights and softening points of the polyamides 2a, 2b and 3a, 3b impede any potential use as a fiber-forming material. However, the copolyamides 4a, 4b and 5a, 5b are more attractive systems for modifying conventional synthetic fibers to improve their hydrophilicity and/or fire-resistance. It is suggested that the strong polar character of the $-\text{P}=\text{O}$ group (ref. 16), along with the amide structure, is responsible for the noticeable hydrophilicity.

The polyamides prepared were thermally characterized through differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Differential Scanning Calorimetry

Typical DSC thermograms are presented in figure 1. A broad endothermic peak was exhibited in most of the DSC thermograms of polyamides between 80° and 180°C , along with a weight loss of $\sim 3\%$ attributed to adsorbed water, despite the fact that the samples were dried in a vacuum oven.

Some of the thermal characteristics of polyamides obtained from their DSC thermograms are listed in table 4. It was impossible to distinguish a glass transition (T_g) or melting (T_m) temperature in the DSC thermograms of some polyamides. However, sharp, reproducible endothermic baseline shifts were obtained for several polyamides that probably correspond to the T_g . In the case of poly(m-phenylene isophthalamide) (6), a T_g value of 250°C was found. Gan et al. (ref. 17) reported a T_g value of 275°C for a polymer of the same structure with an intrinsic viscosity of 1.97 dL/g . The discrepancy is probably due to the adsorbed water and/or the different molecular weights of the polymers. A T_g value of 158°C was found for poly(m-phenylene adipamide)(7), which is in good agreement with the value of 160°C reported in the literature (ref. 18). The T_g values of the copolyamides 4a and 5a are close to those of the corresponding parent polyamides (6) and (7), respectively.

However, the polyamides 2b, 3a, and 3b, having comparatively higher phosphorus contents, have significantly lower Tg values as compared with those of the parent polyamides.

The large endothermic peaks that appeared in the DSC thermograms of several polyamides are attributed to melting. The T_m values obtained from the intersection of the tangent to the front side of the peak with the base line are given in table 4. Because almost every wholly aromatic polyamide that contains neither N-substitution nor ortho-phenylene units begins to decompose near its melting point, determination of the melting temperature is usually very difficult. The use of differential thermal analysis to determine the melting point of such high-melting polymers has become generally accepted as the best technique. From table 4 it can be seen that the copolyamides 4a, 4b and 5a, 5b show lower melting temperatures as compared with the corresponding parent polyamides. Apparently, the reduction of melting temperatures should be attributed to the disruption in chain packing caused by the introduction of the bulky (dialkoxyphosphinyl)methyl group. It should be noted that the introduction of the bulkier [di(2-chloroethoxy)phosphinyl]methyl group resulted in greater reductions of the melting temperatures of the polymers.

The large exothermic peaks observed in the DSC thermograms of the polyamides 2a, 2b and 3a, 3b correspond to their pyrolysis, as confirmed by TGA data. The polyamides 2a and 3a are pyrolyzed at a significantly higher temperature than the corresponding polyamides 2b and 3b.

Thermogravimetric Analysis

Thermogravimetric analytical data of the polyamides in nitrogen are shown in figure 2. The polymer decomposition temperature (PDT), the maximum polymer decomposition temperature (PDT_{max}), the temperature of complete pyrolysis (TCP), and the char yield (percent of residue) at 650°C are shown in table 3. The PDT and the TCP were determined by the intersection of the tangent to the steepest portion of the TGA curve, with the strain-line part of the curve before and after the polymer degradation, respectively. The PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred. From this table it can be seen that all phosphorus-containing polyamides have a lower PDT and a higher char yield than the corresponding common polyamides.

The thermal stability of the polymers decreased steadily with the increasing concentration of the phosphorus-containing sequences in the chains. This may be attributed to the easy thermal dissociation of the phosphorus moieties and the low degree of polymerization of these polymers. As previously mentioned, the polyamides containing [di(2-chloroethoxy)phosphinyl]methyl groups show a significantly lower PDT than those with (diethoxyphosphinyl)methyl groups.

Some TGA data of the polyamides obtained in nitrogen and air atmospheres are shown in table 5. As expected, the synthesized polyamides exhibit a lower thermal stability in air, as compared with that in N₂.

Note that the introduction of the (dialkoxyphosphinyl)methyl group causes the solubility of the polyamides to increase greatly. For example, the poly(m-phenylene isophthalamide)(6) is soluble only in such solvents as concentrated sulphuric acid and formic acid, whereas the polyamides 2a, 2b are soluble in solvents such as chloroform and acetone. The greater solubility range of the phosphorus-containing polyamides over the common polyamides is probably due to the lower molecular weights and their

amorphous characters. The lack of crystallinity in polyamides 2a, 2b and 3a, 3b may be attributed to the bulkiness of the (dialkoxyposphinyl)methyl groups and to the subsequent disruption in chain packing. Certain high-molecular-weight wholly aromatic polyamides are difficult, or even impossible, to fabricate because of their poor solubility (ref. 19). Therefore, the increased solubility of the polyamides which results from incorporating the (dialkoxyposphinyl)methyl group is important from a technological point of view.

Limiting Oxygen Index Values

The fire-resistance of some polyamides was evaluated by determining their limiting oxygen index (LOI) values. The LOI values determined, and the content of the polymers in phosphorus and chlorine, are shown in table 6. It can be seen that the phosphorus-containing polyamides show a significantly higher degree of fire-resistance than the corresponding common polyamides. However, the significance of these LOI data should not be overemphasized, because the low molecular weight of the phosphorus-containing polyamides may have contributed to the high LOI values by permitting low-viscosity melts to drip during burning. The role of dripping in obtaining high LOI values was demonstrated earlier for polyamides (ref. 20).

Furthermore, it was shown that the polyamides 2a, 2b and 3a, 3b may be used as an additive or for melt-blending with common polyamides to increase their fire-resistance. Specifically, the polyamide 2a was used as a fire-retardant additive to (6). For this purpose, powder of 2a was mixed with powder of (6) in various proportions. The specimens were formed by hot-pressing the mixtures in a mold, and the LOI values were determined. The results are shown in table 7, and plotted in figure 3.

As shown on table 6, the copolyamide 4a contained 1.44% P and had an LOI value of 52.0. It can be seen from table 7 that a blend of polyamides 2a and (6) which contained 1.46% P exhibited an LOI value of 51.6. Thus, the efficiency of the (dialkoxyposphinyl)methyl groups is higher when they are an inherent part of the polymer chain, rather than the component of a physical mixture.

EXPERIMENTAL

General

A Varian EM-390 NMR spectrometer at 90 MHz was used to record the ^1H -NMR spectra. Chemical shifts (δ) are given in parts per million with tetramethylsilane as an internal standard. A Nicolet FT-IR spectrometer with KBr pellets was used to record IR spectra. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed using a DuPont 1090 Thermal Analyzer. Measurements were made at a heating rate of $20^\circ\text{C}/\text{min}$ in atmospheres of N_2 or air at a flow rate of $80\text{ cm}^3/\text{min}$.

The limiting oxygen index (LOI) of the polyamides was determined with a Stanton Redcroft flammability unit (ASTM D 2863-74). The LOI specimens measuring $70 \times 6.5\text{ mm}$ were formed by hot-pressing polyamide powder in a mold. The mixture of nitrogen and oxygen passed upward through the chimney at a flow rate of $18\text{ L}/\text{min}$.

Elemental analyses were performed by Huffman Laboratories, Inc., Wheat Ridge, Colorado.

Reagents and Solvents

The dihydrochloride salt of 1-[(diethoxyphosphonyl)methyl]-2,4- and -2,6-dinitrobenzene (DEPD) was purified by washing with acetone. It decomposed at temperatures higher than 128°C. 1-[(di(2-chloroethoxyphosphonyl)methyl)-2,4- and -2,6-diaminobenzene (DCEPD) was purified by recrystallization from benzene (m.p. 116-119°C). Commercial-grade dihydrochloride salt of m-phenylenediamine was used. Isophthaloyl dichloride was recrystallized from n-hexane. Adipoyl dichloride and pyridine were distilled under reduced pressure. N,N-dimethylacetamide (DMAC) was dried by refluxing and fractionally distilled from calcium hydride.

Preparation of Phosphorus-Containing Polyamides and Copolyamides

Preparation of the Polyamides 2a and 2b- Dihydrochloride salt of DEPD (6.29 g, 19.0 mmol), 60 ml of DMAC and pyridine (6.01 g, 76.0 mmol) were placed in a three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a nitrogen inlet. The mixture was stirred to dissolve the dihydrochloride salt of DEPD and cooled to 0-1°C. A solution of isophthaloyl dichloride (3.86 g, 19.0 mmol) in 30 mL of DMAC was added by drops in a nitrogen atmosphere. The reaction took place for 10 min in an ice bath, followed by 60 min at room temperature. The mixture was poured into about 600 ml of methanol, and the resulting precipitate was filtered, washed repeatedly with methanol, and dried at 80°C in a vacuum oven. Polyamide 2a was obtained in an 82% yield (6.05 g).

In a likewise manner, polyamide 2b was prepared by reacting DCEPD (3.28 g, 10.0 mmol) with isophthaloyl dichloride (2.04 g, 10.0 mmol) in the presence of pyridine (1.59 g, 20.0 mmol). The yield was 85% (3.90 g).

Preparation of the Copolyamides 4a and 4b- Dihydrochloride salt of DEPD (2.21 g, 6.7 mmol), dihydrochloride salt of m-phenylenediamine (6.21 g, 34.3 mmol), and pyridine (12.96 g, 163.8 mmol) were dissolved in 80 mL of DMAC. When isophthaloyl dichloride (8.32 g, 41.0 mmol), dissolved in 60 ml of DMAC, was added to the above solution, the mixture reacted as did the 2a polyamide. Copolyamide 4a was obtained in a 90% yield (9.70 g).

The same procedure used to obtain 4a was used to obtain 4b; DCEPD (2.99 g, 9.1 mmol) and dihydrochloride salt of m-phenylenediamine (5.81 g, 32.0 mmol) reacted with isophthaloyl dichloride (8.37 g, 41.2 mmol) in the presence of pyridine (11.59 g, 146.5 mmol). The yield was 94% (11.10 g).

Preparation of the Polyamides 3a and 3b- DEPD was formed in situ by adding pyridine (7.24 g, 91.6 mmol) to the dihydrochloride salt of DEPD (7.58 g, 22.9 mmol) in 60 mL of DMAC. Adipoyl dichloride (4.19 g, 22.9 mmol), diluted with 30 mL of DMAC, was added to this solution while it was stirred in a nitrogen atmosphere at 0-1°C. The mixture was subsequently stirred for 60 min at room temperature and poured into water. The resulting precipitate was dried overnight at 90°C in a vacuum oven. Polyamide 3a was obtained in an 81% yield (6.83 g).

In a likewise manner, polyamide 3b was prepared by reacting DCEPD (3.36 g, 10.3 mmol) with adipoyl dichloride (1.88 g, 10.3 mmol) in the presence of pyridine (1.62 g, 20.5 mmol). The yield was 76% (3.41 g).

Preparation of the Copolyamides 5a and 5b- Dihydrochloride salt of DEPD (2.94 g, 8.9 mmol), dihydrochloride salt of m-phenylenediamine (8.78 g, 48.0 mmol), and

pyridine (18.00 g, 227.6 mmol) were dissolved in 100 mL of DMAC. When adipoyl dichloride (10.41 g, 56.9 mmol), diluted with 40 ml of DMAC, was added to the above solution, the mixture reacted as did the 3a polyamide. The copolyamide 5a was obtained in an 84% yield (11.55 g).

Similarly, copolyamide 5b was prepared by reacting DCEPD (2.91 g, 8.9 mmol) and dihydrochloride salt of m-phenylenediamine (6.16 g, 34.0 mmol) with adipoyl dichloride (7.85 g, 42.9 mmol) in the presence of pyridine (12.16 g, 153.8 mmol). The reaction yield was 81% (9.16 g).

CONCLUSIONS

Polyamides obtained by the reaction of the compounds (R.1) with an acid chloride, such as isophthaloyl dichloride or adipoyl dichloride, had relatively low molecular weights. Copolyamides obtained by the reaction of (1) and m-phenylenediamine with the previously mentioned acid chlorides yielded somewhat higher molecular weights. The infrared spectra of the phosphorus-containing polyamides illustrate the characteristic absorption bands of P=O and P-O-C groups. In addition, the structure of the polymers was verified by elemental analysis and ¹H-NMR spectroscopy. The phosphorus-containing polyamides were thermally characterized by DSC and TGA, and their properties were compared with those of the corresponding common polyamides. The Tg and Tm values of the polymers are decreased with increasing concentration of the phosphorus moieties. The phosphorus-containing polyamides indicated at lower PDT and a higher char yield than the corresponding common polyamides. In addition, the common polyamides exhibited a considerably lower degree of fire resistance than did the phosphorus-containing polyamides.

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TABLE 1.- ELEMENTAL ANALYSIS OF POLYAMIDES

| Polymer | Formula | Elemental analysis, % | | | | |
|---------|---------------------------|-------------------------------|----------------|------------------|----------------|----------------|
| | | C | H | Cl | N | P |
| 2a | $C_{19}H_{21}N_2O_5P$ | 58.46 (58.78) ^a | 5.46 (5.41) | | 6.93 (7.22) | 7.66 (7.98) |
| 2b | $C_{19}H_{19}Cl_2N_2O_5P$ | 49.69 (49.92) | 4.26 (4.16) | 15.39 (15.51) | 5.92 (6.13) | 6.60 (6.78) |
| 4a | | | | | | 1.44 (1.92) |
| 4b | | | | 5.14 (5.48) | | 2.09 (2.39) |
| 3a | $C_{17}H_{25}N_2O_5P$ | 55.14 (55.46) | 6.99 (6.79) | | 7.23 (7.61) | 7.93 (8.41) |
| 3b | $C_{17}H_{23}Cl_2N_2O_5P$ | 46.98 (46.71) | 5.12 (5.26) | 16.10 (16.23) | 6.87 (6.41) | 7.10 (7.09) |
| 5a | | | | | | 1.52 (2.00) |
| 5b | | | | 4.84 (5.81) | | 2.04 (2.54) |

^aNumbers in parentheses indicate the calculated values.

TABLE 2.- PHYSICAL CHARACTERISTICS OF POLYAMIDES

| Polymer | IR | ¹ H-NMR | |
|---------|---|---------------------|--|
| | KBr, cm ⁻¹ | Solvent | PPM |
| 2a | 3370-3160 (NH stretching); 1675 (C=O); 1604 (aromatic); 1523 (NH deformation); 1245-1215 (P=O); 1048-963 (P-O-C) | DMSO-d ₆ | 8.67-7.37 (m, 7H, aromatic); 3.97 (m, 4H, CH ₃ CH ₂ O); 3.45 (d, J _{PCH} = 22 Hz, 2H, PCH ₂); 1.15 (t, 6H, CH ₃ CH ₂ O) |
| 2b | 3375-2963 (NH stretching); 1671 (C=O); 1604 (aromatic); 1524 (NH deformation); 1247 (P=O); 1078-1022 (P-O-C); 722, 668 (C-Cl) | DMSO-d ₆ | 8.75-7.56 (m, 7H, aromatic); 4.33 (m, 4H, ClCH ₂ CH ₂ O); 3.90 (m, 4H, ClCH ₂ CH ₂ O); 3.67 (d, J _{PCH} = 22 Hz, 2H, PCH ₂) |
| 4a | 3475-3175 (NH stretching); 1655 (C=O); 1606 (aromatic); 1534 (NH deformation); 1243 (P=O); 1046-1023 (P-O-C) | | |
| 4b | 3400-3175 (NH stretching); 1659 (C=O); 1606 (aromatic); 1535 (NH deformation); 1242 (P=O); 1079-1021 (P-O-C); 719, 686 (C-Cl) | | |
| 3a | 3375-3175 (NH stretching); 2930, 2865 (CH ₂ stretching); 1669 (C=O); 1604 (aromatic); 1528 (NH deformation); 1220 (P=O); 1051-961 (P-O-C) | DMSO-d ₆ | 7.80-7.20 (m, 3H, aromatic); 3.93 (m, 4H, CH ₃ CH ₂ O); 3.23 (d, J _{PCH} = 22 Hz, 2H, PCH ₂); 2.33 (broad, 4H, COCH ₂); 1.67 (broad, 4H, CH ₂); 1.13 (t, 6H, CH ₃ CH ₂ O) |
| 3b | 3375-3175 (NH stretching); 2930, 2865 (CH ₂ stretching); 1684-1669 (C=O); 1602 (aromatic); 1528 (NH deformation); 1225 (P=O); 1077-1020 (P-O-C); 732, 667 (C-Cl) | DMSO-d ₆ | 7.87-7.17 (m, 3H, aromatic); 4.10 (m, 4H, ClCH ₂ CH ₂ O); 3.73 (m, 4H, ClCH ₂ CH ₂ O); 3.37 (d, J _{PCH} = 22 Hz, 2H, PCH ₂); 2.37 (broad, 4H, COCH ₂); 1.53 (broad, 4H, CH ₂) |
| 5a | 3375-3175 (NH stretching); 2947, 2868 (CH ₂ stretching); 1662 (C=O); 1606 (aromatic); 1535 (NH deformation); 1220 (P=O); 1051-961 (P-O-C) | | |
| 5b | 3375-3175 (NH stretching); 2947, 2868 (CH ₂ stretching); 1665 (C=O); 1606 (aromatic); 1536 (NH deformation); 1220 (P=O); 1077-1023 (P-O-C); 729, 668 (C-Cl) | | |

TABLE 3.- VALUES OF INHERENT VISCOSITY, PHOSPHORUS CONTENT, AND THERMAL STABILITY OF POLYAMIDES IN N₂ ATMOSPHERE

| Polyamide | n _{inh} ^a | P, % | Temperature, °C | | | Char yield, % residue at 650°C |
|-----------|-------------------------------|------|-----------------|--------------------|-----|--------------------------------|
| | | | PDT | PDT _{max} | TCP | |
| 2a | 0.14 | 7.66 | 329 | 373 | 550 | 76 |
| 2b | .16 | 6.60 | 258 | 289 | 450 | 60 |
| 4a | .22 ^b | 1.44 | 430 | 480 | 630 | 73 |
| 4b | .33 | 2.09 | 340 | 450 | 640 | 66 |
| 6 | .47 ^b | 0 | 455 | 527 | 645 | 60 |
| 3a | .10 | 7.93 | 311 | 364 | 500 | 51 |
| 3b | .11 | 7.10 | 215 | 253 | 377 | 51 |
| 5a | .31 | 1.52 | 391 | 431 | 499 | 54 |
| 5b | .34 | 2.04 | 332 | 398 | 461 | 51 |
| 7 | .36 ^b | 0 | 411 | 463 | 509 | 34 |

^a0.5 g/dL in N,N-dimethylformamide at 25°C.

^b0.5 g/dL in concentrated H₂SO₄ at 25°C.

TABLE 4.- SOME THERMAL CHARACTERISTICS OF POLYAMIDES

| Polyamide | Tg, °C | Tm, °C |
|-----------|------------------|------------------|
| 2a | 204 | 287 |
| 2b | 174 | --- ^a |
| 4a | 256 | 286 |
| 4b | --- ^a | 260 |
| 6 | 250 | 387 |
| 3a | 164 | --- ^a |
| 3b | 150 | --- ^a |
| 5a | 166 | 206 |
| 5b | --- ^a | 158 |
| 7 | 158 | 216 |

^aA transition temperature cannot be distinguished.

TABLE 5.- TGA DATA OF POLYAMIDES

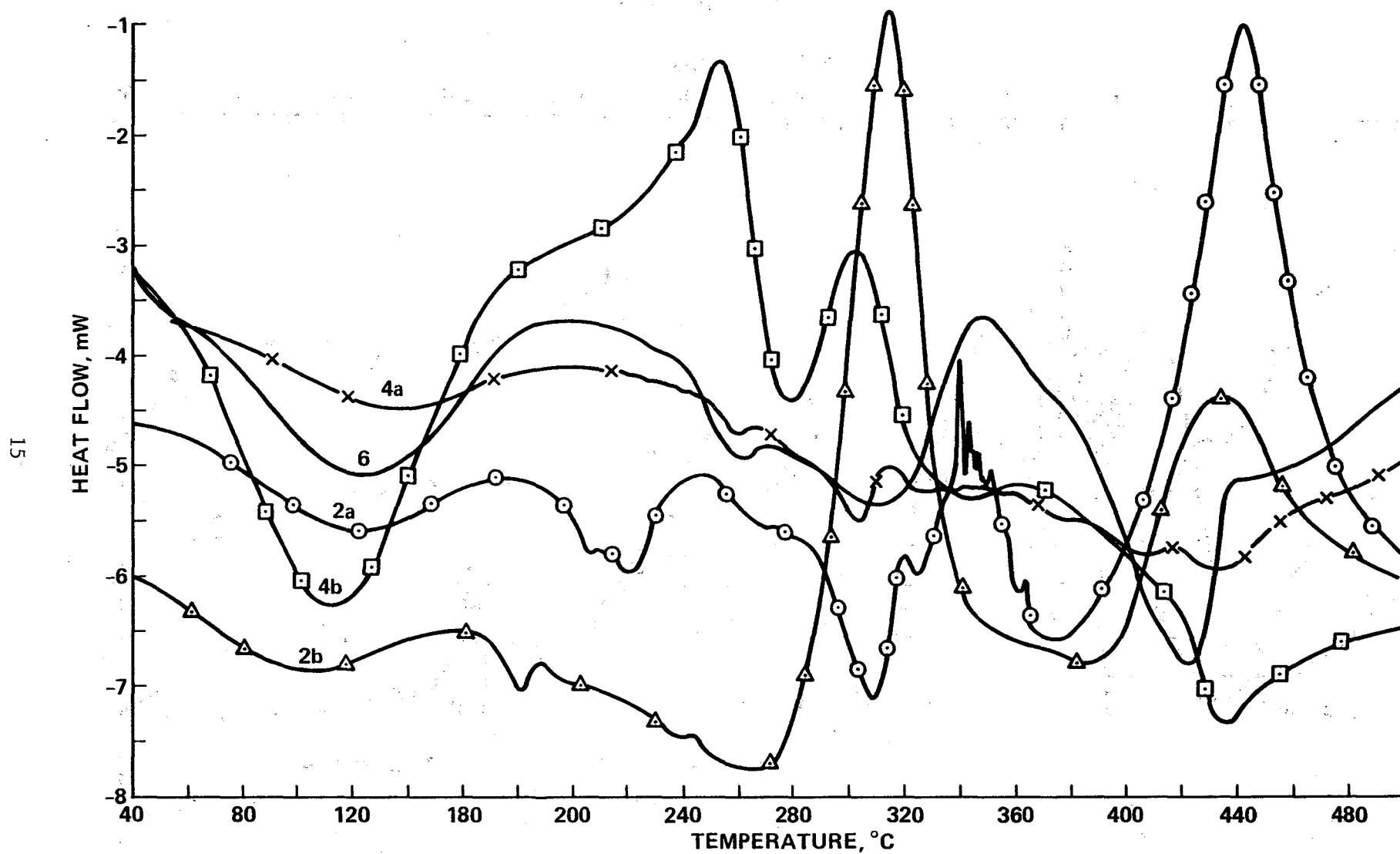
| Polyamide | Weight loss in nitrogen, % | | | Weight loss in air, % | | |
|-----------|-------------------------------|-------|-------|--------------------------|-------|-------|
| | 400°C | 550°C | 700°C | 400°C | 550°C | 700°C |
| 2a | 11 | 21 | 27 | 17 | 26 | 60 |
| 2b | 26 | 35 | 43 | 26 | 42 | 60 |
| 4a | 5 | 22 | 29 | 4 | 22 | 79 |
| 4b | 14 | 27 | 41 | 12 | 71 | 97 |
| 6 | 10 | 30 | 43 | 4 | 20 | 94 |
| 3a | 25 | 46 | 50 | 20 | 33 | 59 |
| 3b | 35 | 48 | 50 | 34 | 45 | 70 |
| 5a | 9 | 43 | 46 | 6 | 32 | 70 |
| 5b | 27 | 47 | 50 | 20 | 45 | 84 |
| 7 | 8 | 64 | 67 | 5 | 53 | 96 |

TABLE 6.- FIRE-RESISTANCE
OF POLYAMIDES

| Polyamide | P, % | Cl, % | LOI |
|-----------|------|-------|------|
| 4a | 1.44 | 0 | 52.0 |
| 4b | 2.09 | 5.14 | 52.6 |
| 6 | 0 | 0 | 46.4 |
| 5a | 1.52 | 0 | 45.0 |
| 5b | 2.04 | 4.84 | 45.7 |
| 7 | 0 | 0 | 29.4 |

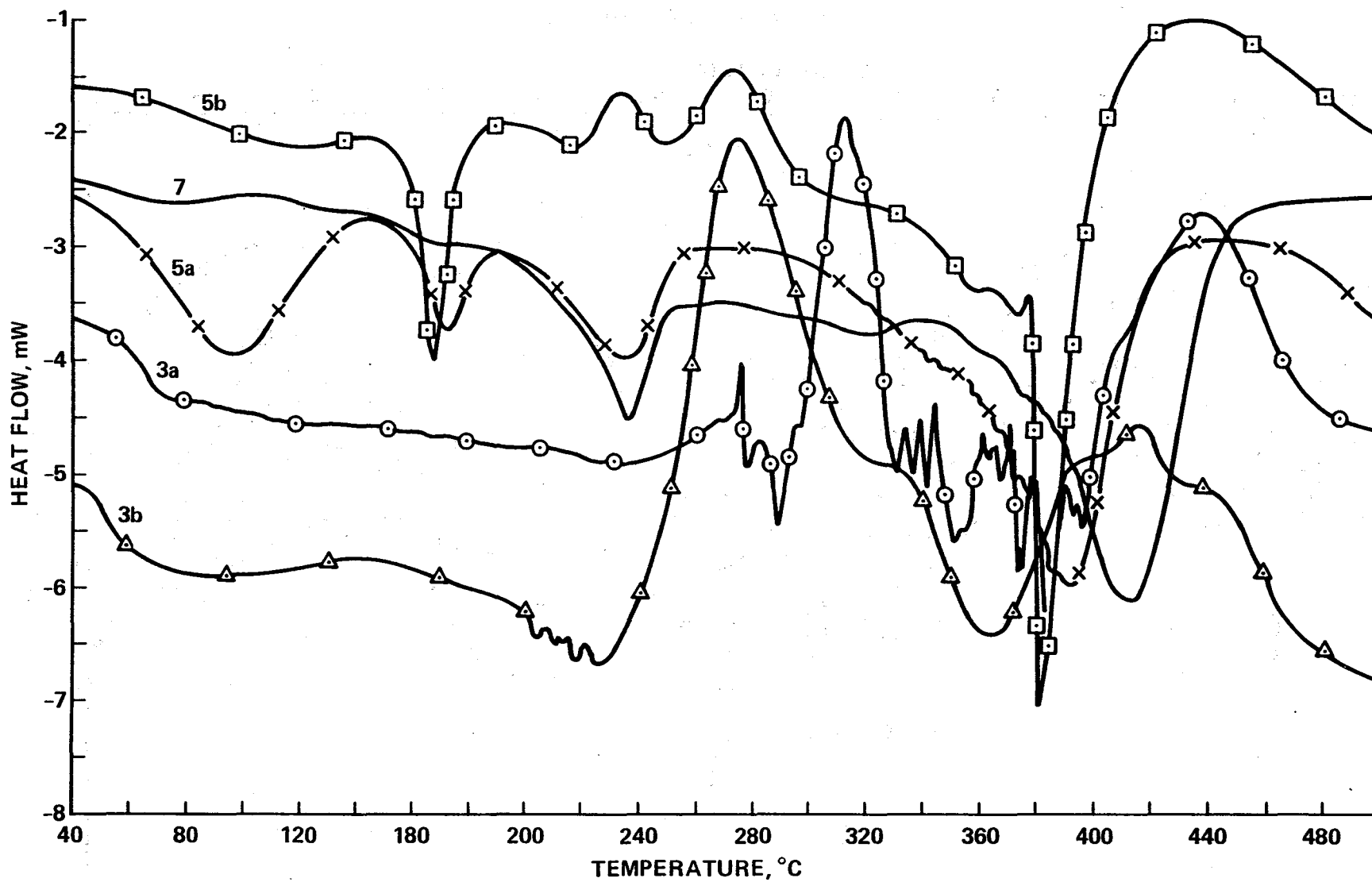
TABLE 7.- LIMITING OXYGEN INDEX OF BLENDS OF POLYAMIDES 2a and (6)

| | | | | | | |
|--------------------------|------|------|------|-------|-------|-------|
| Phosphorus in blend, % | 0 | 0.24 | 0.48 | 0.95 | 1.46 | 1.90 |
| Polyamide 2a in blend, % | 0 | 3.75 | 7.50 | 15.00 | 23.00 | 30.00 |
| LOI | 46.4 | 49.0 | 50.9 | 51.2 | 51.6 | 53.6 |



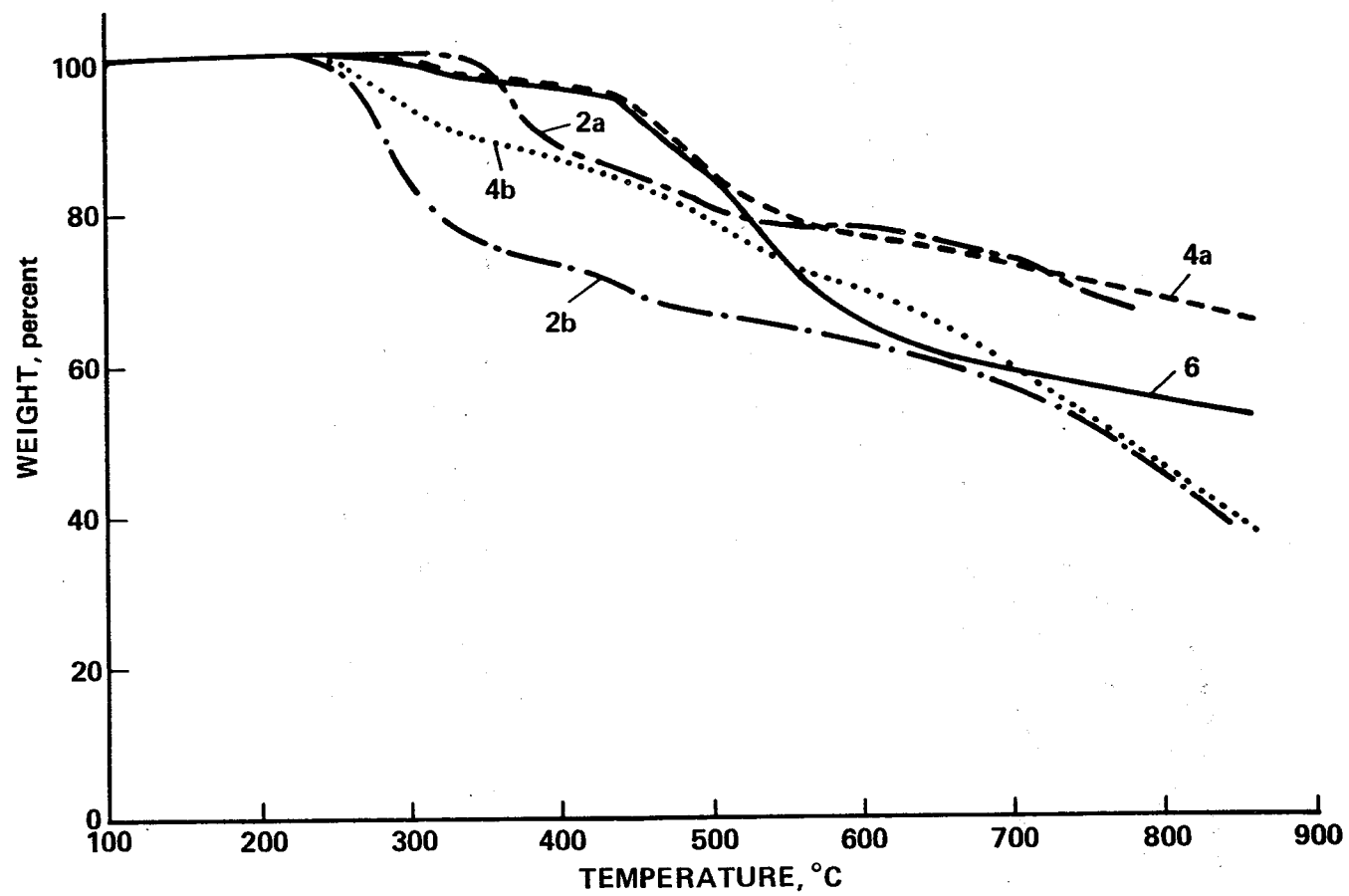
(a) Polyamides 2, 4, and 6.

Figure 1.- Differential scanning calorimetry thermograms of polyamides in N_2 .



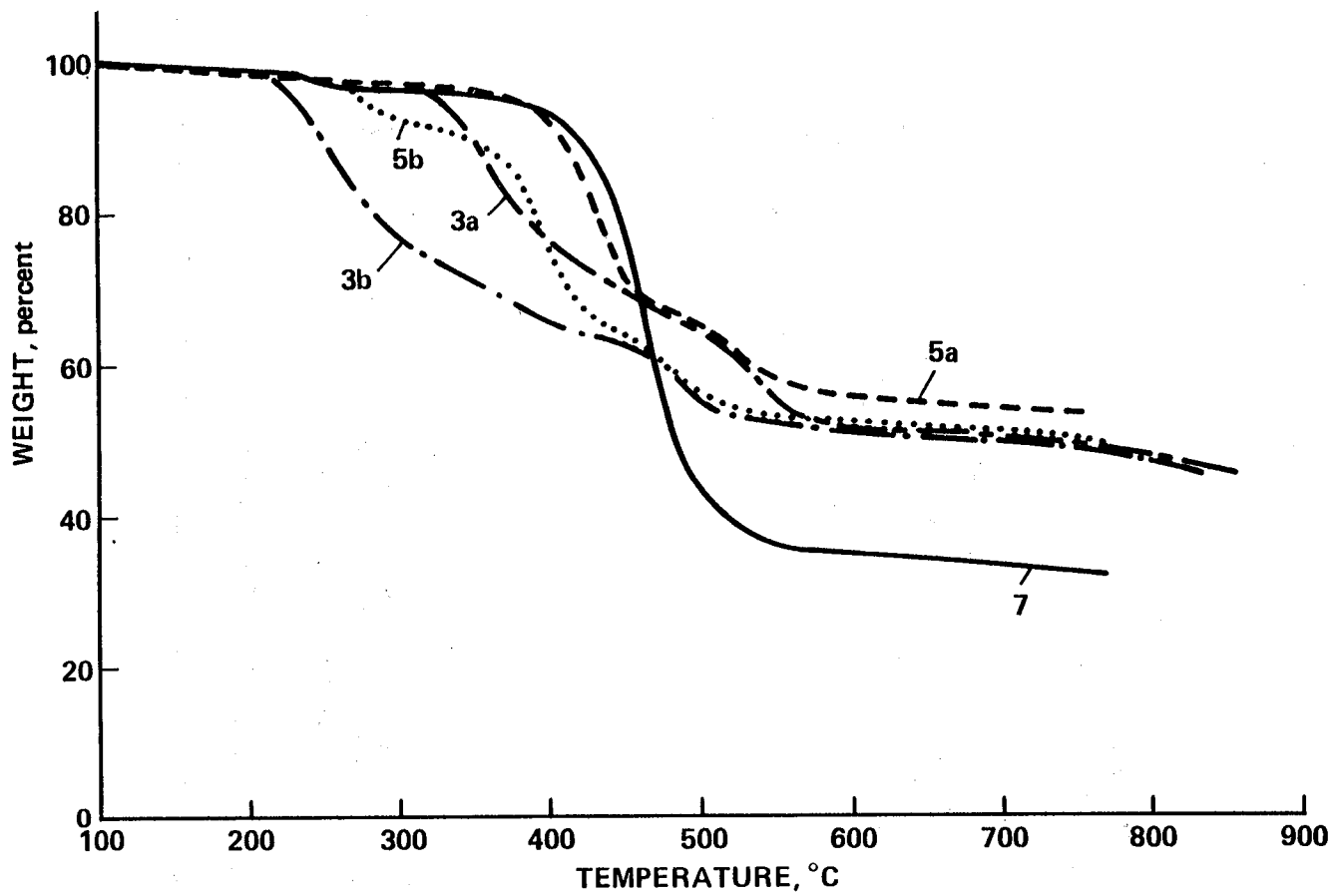
(b) Polyamides 3, 5, and 7.

Figure 1.- Concluded.



(a) Polyamides 2, 4, and 6.

Figure 2.- Thermogravimetric analysis thermograms of polyamides in N_2 .



(b) Polyamides 3, 5, and 7.

Figure 2.- Concluded.

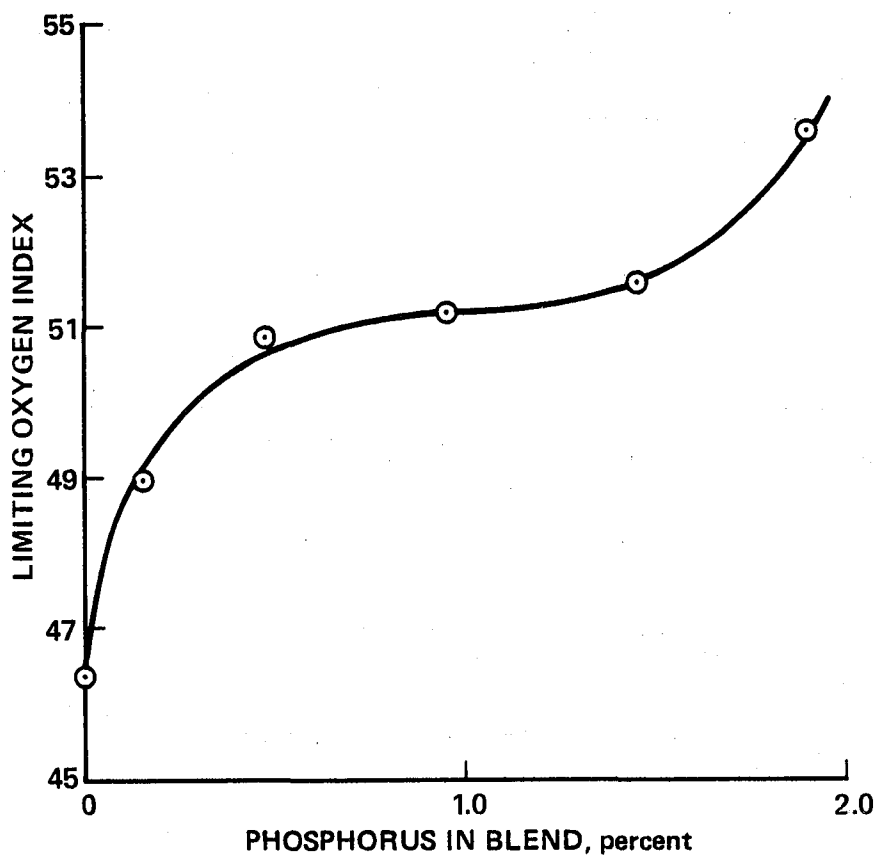


Figure 3.- Limiting oxygen index of blends of polyamides 2a and (6) as a function of phosphorus content in the blends.

| | | | | | |
|--|--|--|--|--|--|
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| 16. Abstract Phosphorus-containing polyamides and copolyamides were prepared from 1-[(dialkoxyphosphinyl)methyl]-2,4- and -2,6-diaminobenzenes. The polymers produced were characterized by infrared and proton nuclear magnetic resonance spectroscopy, differential scanning calorimetry, and thermogravimetric analysis. Their thermal properties were compared with those of the corresponding common polyamides. In addition, by determining the limiting oxygen index value of some of these polyamides, their fire-resistance was evaluated. | | | | | |
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